Structural Studies of Porphyrin Derivatives

K. Barkigia and M. Renner (BNL)

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Introduction: Porphyrins are tetrapyrrole derivatives that mediate a spectrum of bioenergetic reactions ranging from photosynthetic solar energy transduction to conversion of carbon dioxide into fuel. Their structures have been widely studied to ascertain the factors that control bioenergetic and catalytic reactions. Of interest to us are the radicals that are generated during the course of these reactions. They are oxidized porphyrins in which an electron has been removed from the macrocycle rather than the metal. Over the past year, we have determined the structures of several new porphyrin radicals. In addition, we have solved the structures of new photosensitzers for photodynamic therapy, self-assembled hydrogen-bonded porphyrin aggregates and an ensemble of catalytic porphyrins whose peripheral substituents drastically alter their redox properties. Since these compounds are generally prepared by small-scale syntheses and are often reactive toward light and oxygen, use of the NSLS allows fast data collection on very small crystals. Such studies would have been impossible on a conventional diffractometer.

Methods and Materials: For each compound, at least two hemispheres of data were collected at liquid nitrogen temperature by the rotation method using a MAR345 image detector. The data were processed and merged with Denzo/Scalepack (Z. Otwinowski and W. Minor, 1997) and the structures were refined with the SHELXTL package (G. Sheldrick, 1995).

Results: The derived esds on the Zn-N and Zn-O distances are 0.004 and 0.005D, respectively for 1 Final values of R1 and wR2 are 0.079 and 0.195 for 2028 observed reflections. Several crystals of known radicals, such as 1 (H. Song *et al.*, 1990) were examined to check their integrity for future electron density mapping experiments.

Conclusions: The structures form the basis for theoretical calculations that serve to test theoretical treatments and to predict the properties of new porphyrins *a priori*.

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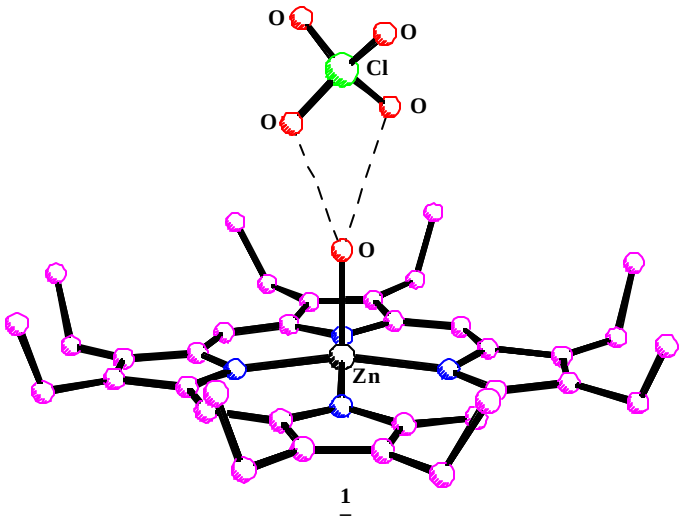

Figure 1. The structure of a Zn cation radical. The counterion is perchlorate, which hydrogen bonds through two of its oxygens to the porphyrins's axial water ligand. The hydrogen bonds between the water and perchlorate are indicated by dashed lines. All hydrogens have been omitted for clarity.